

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number  
**WO 01/61330 A2**

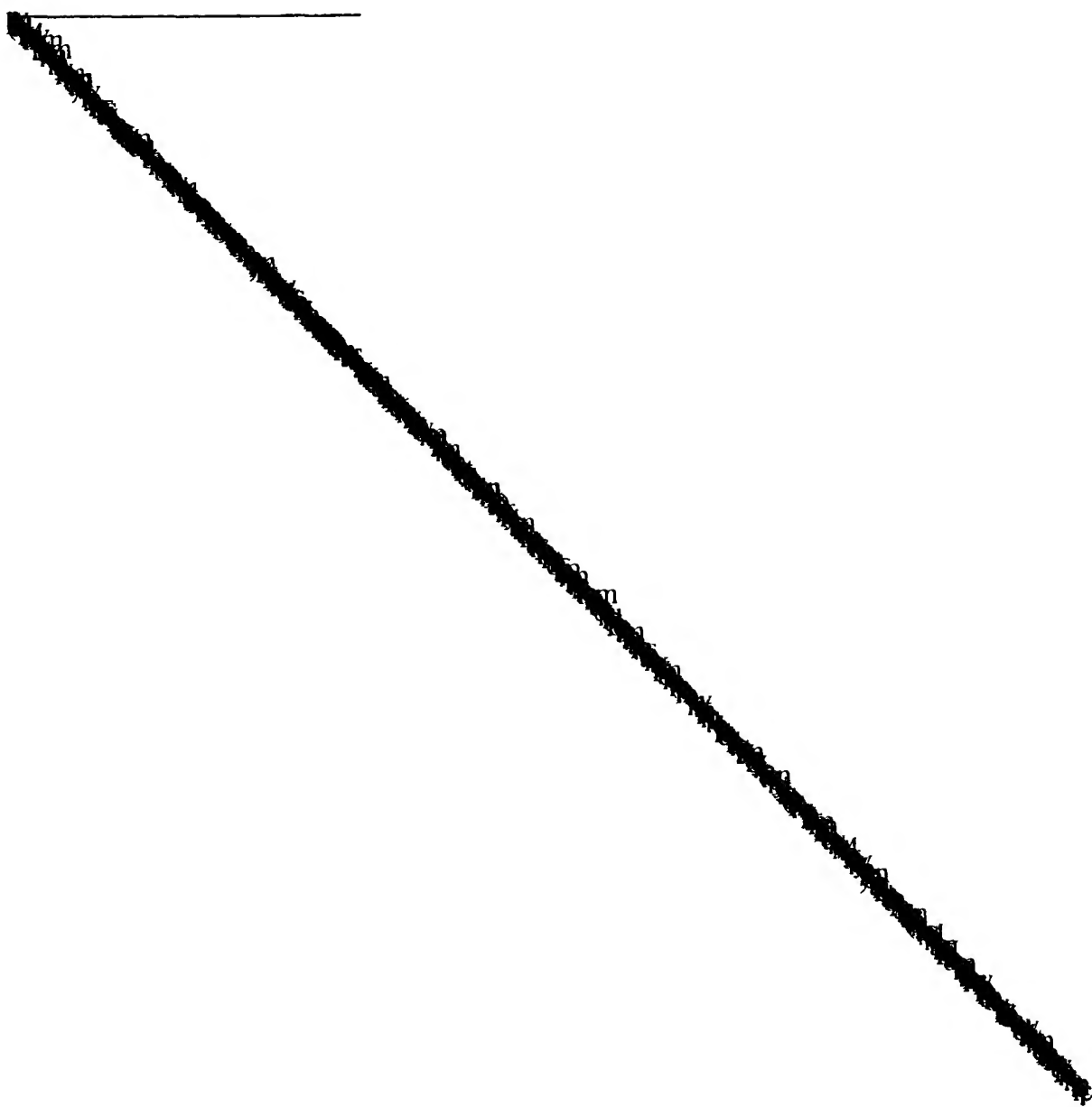
- (51) International Patent Classification<sup>7</sup>: **G01N 27/00**
- (21) International Application Number: **PCT/IL01/00152**
- (22) International Filing Date: 19 February 2001 (19.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
134631 20 February 2000 (20.02.2000) IL
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **CONSTRUCTIVE NANOLITHOGRAPHY**

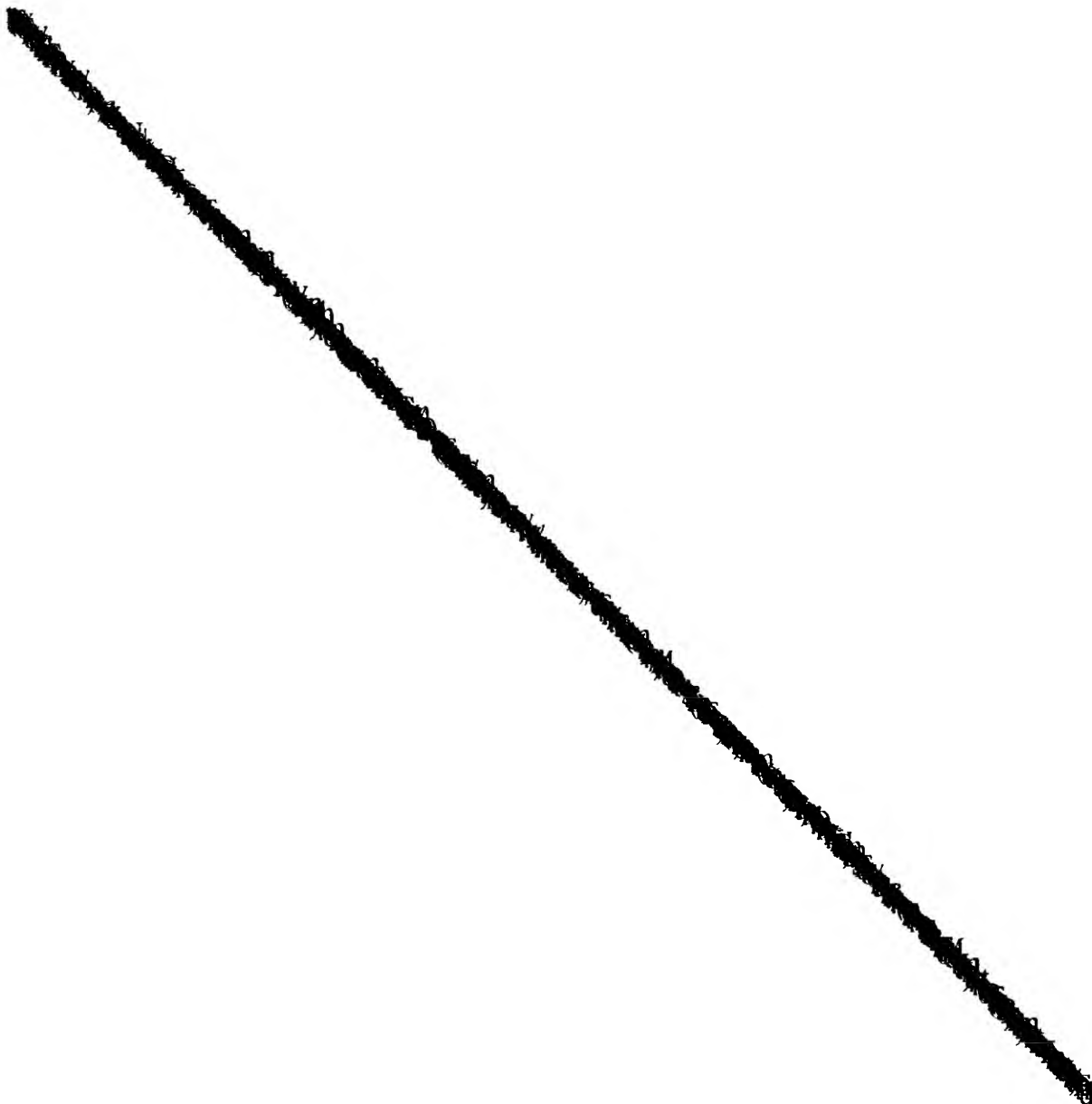
(57) Abstract: A patterned organic monolayer or multilayer film self-assembled on a solid substrate, the pattern consisting in a site-defined surface chemical modification non-destructively inscribed in the organic monolayer or multilayer by means of an electrically biased conducting scanning probe device, stamping device and/or liquid metal or metal alloy or any other device that can touch the organic monolayer or multilayer surface and inscribe therein a chemical modification pattern upon application of an electrical bias.

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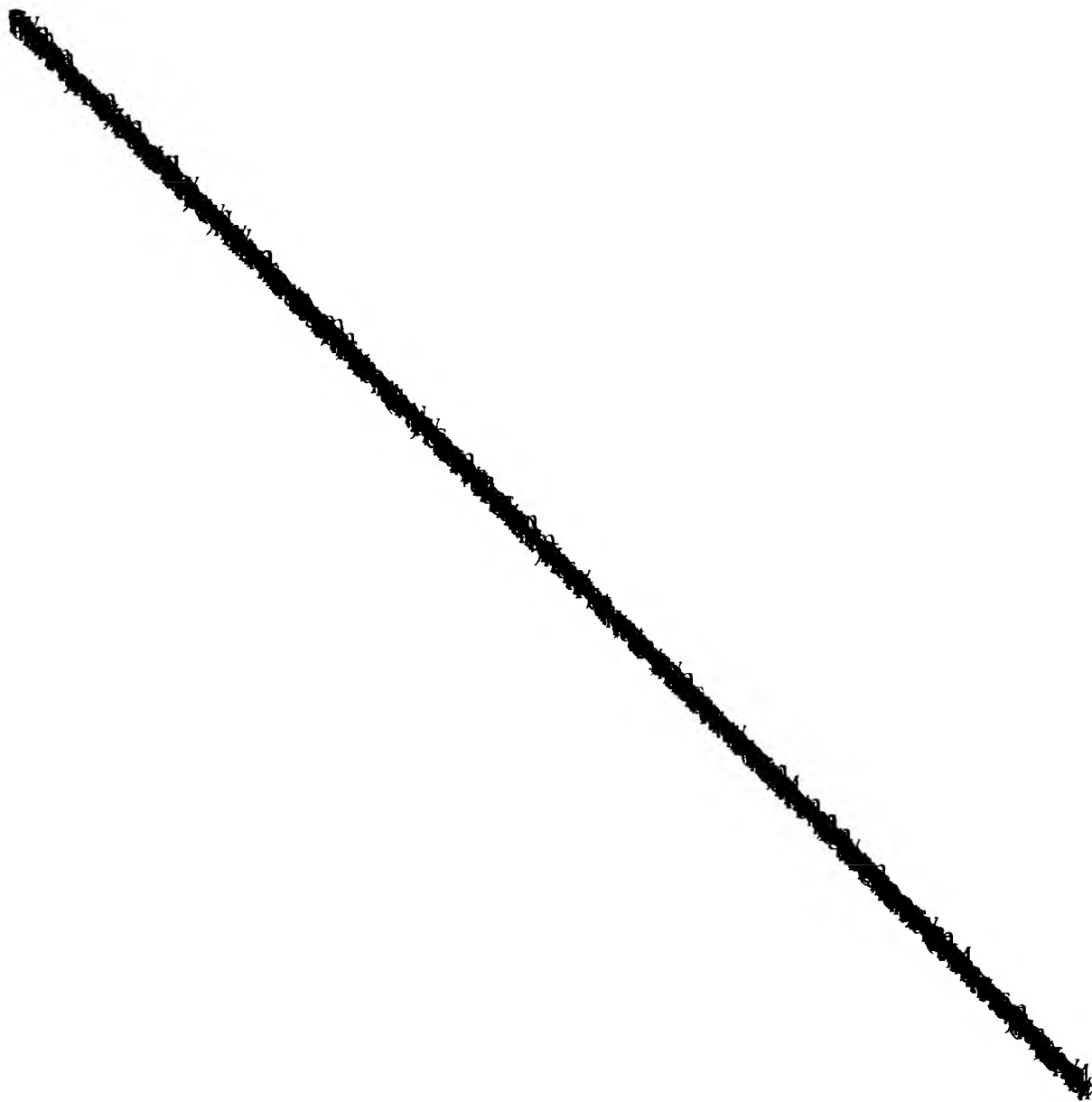
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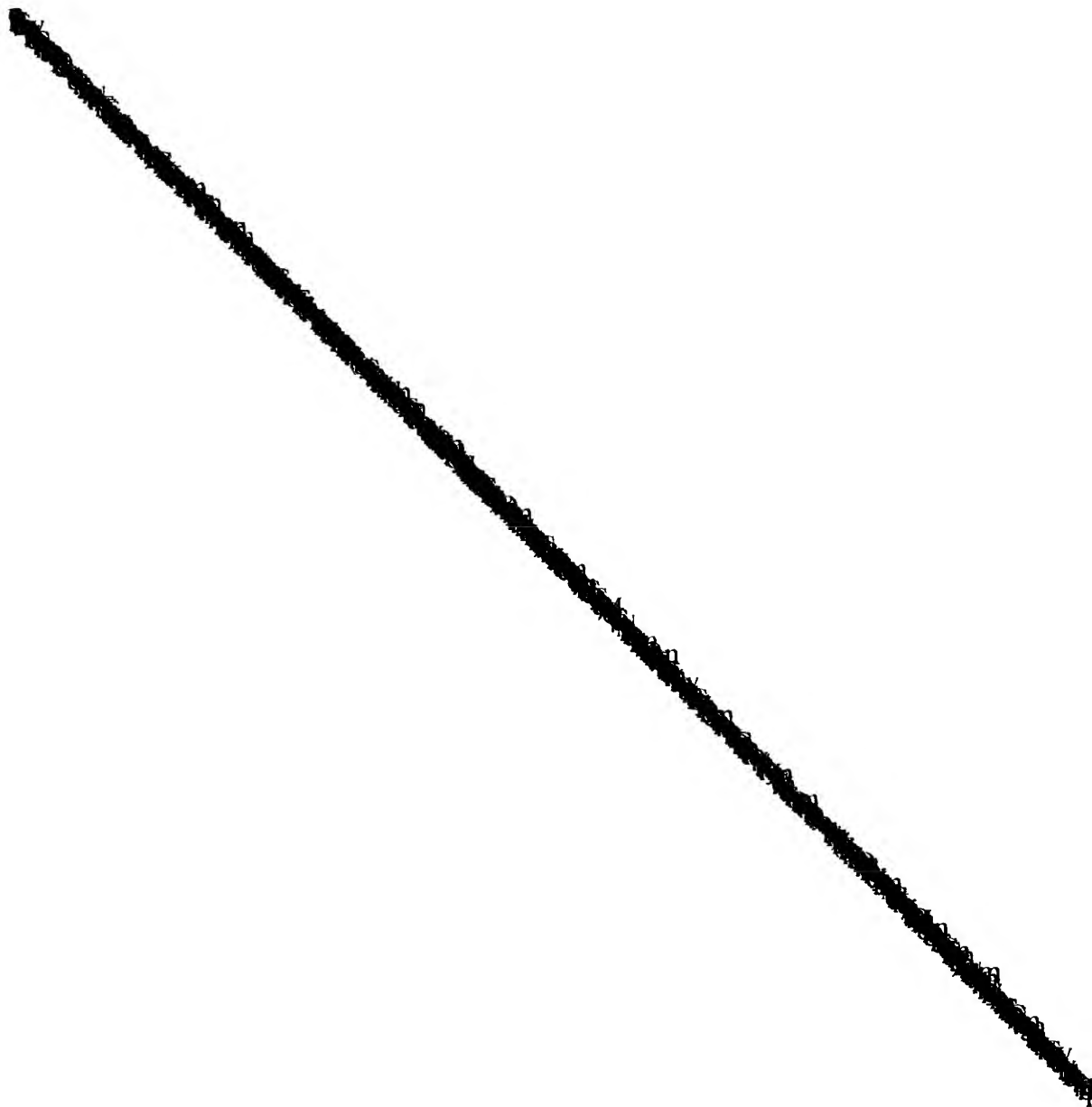
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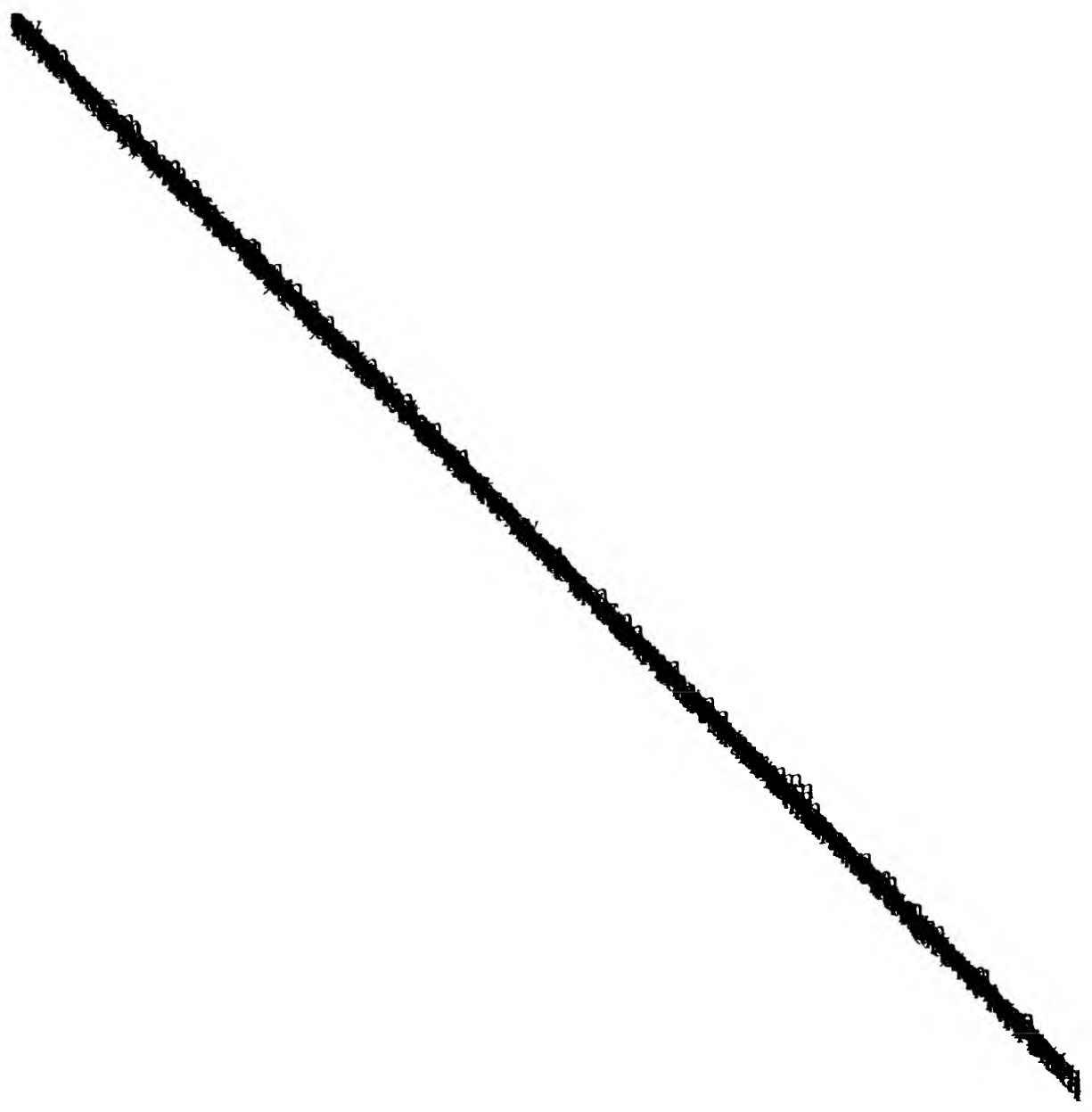
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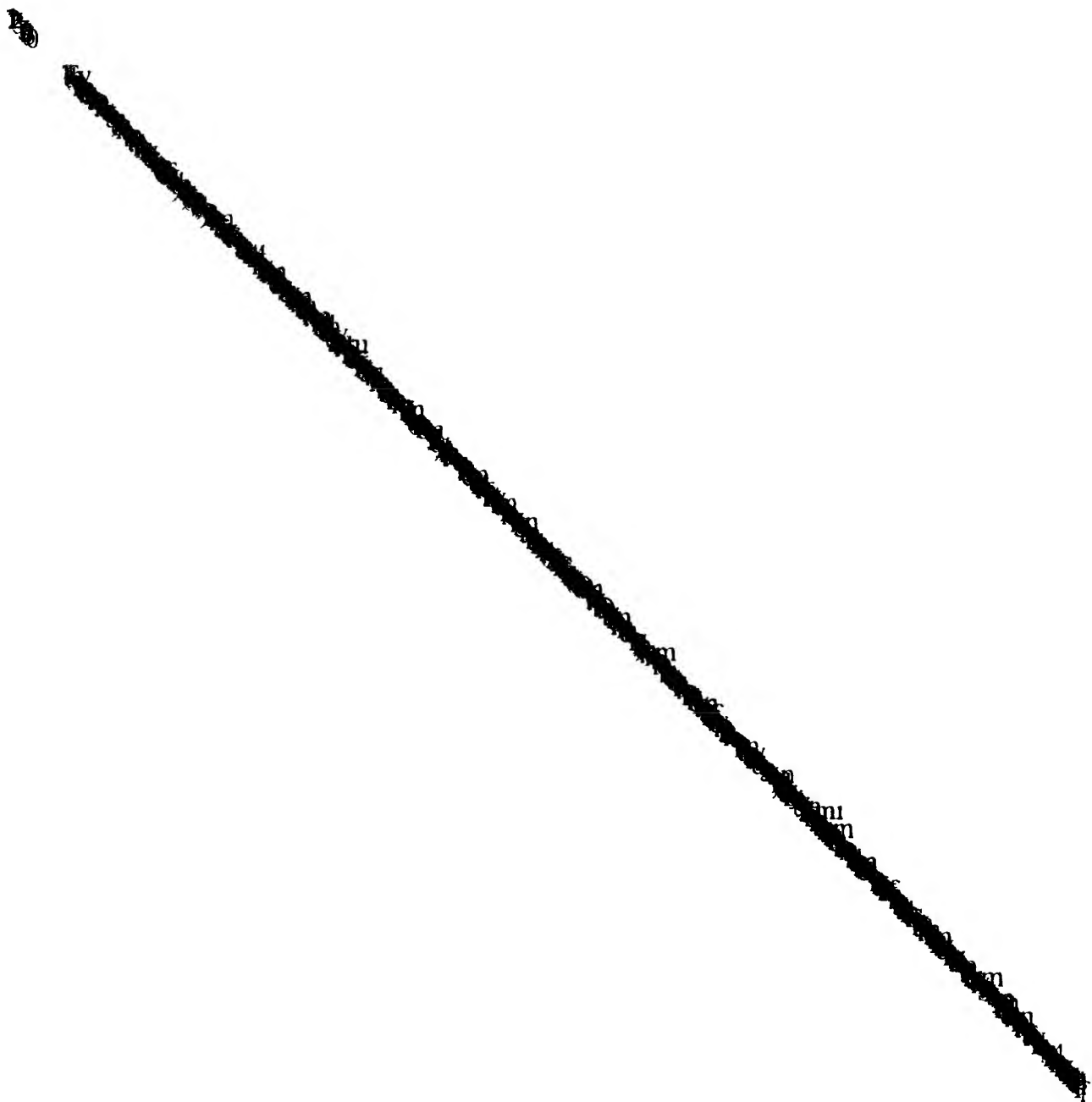


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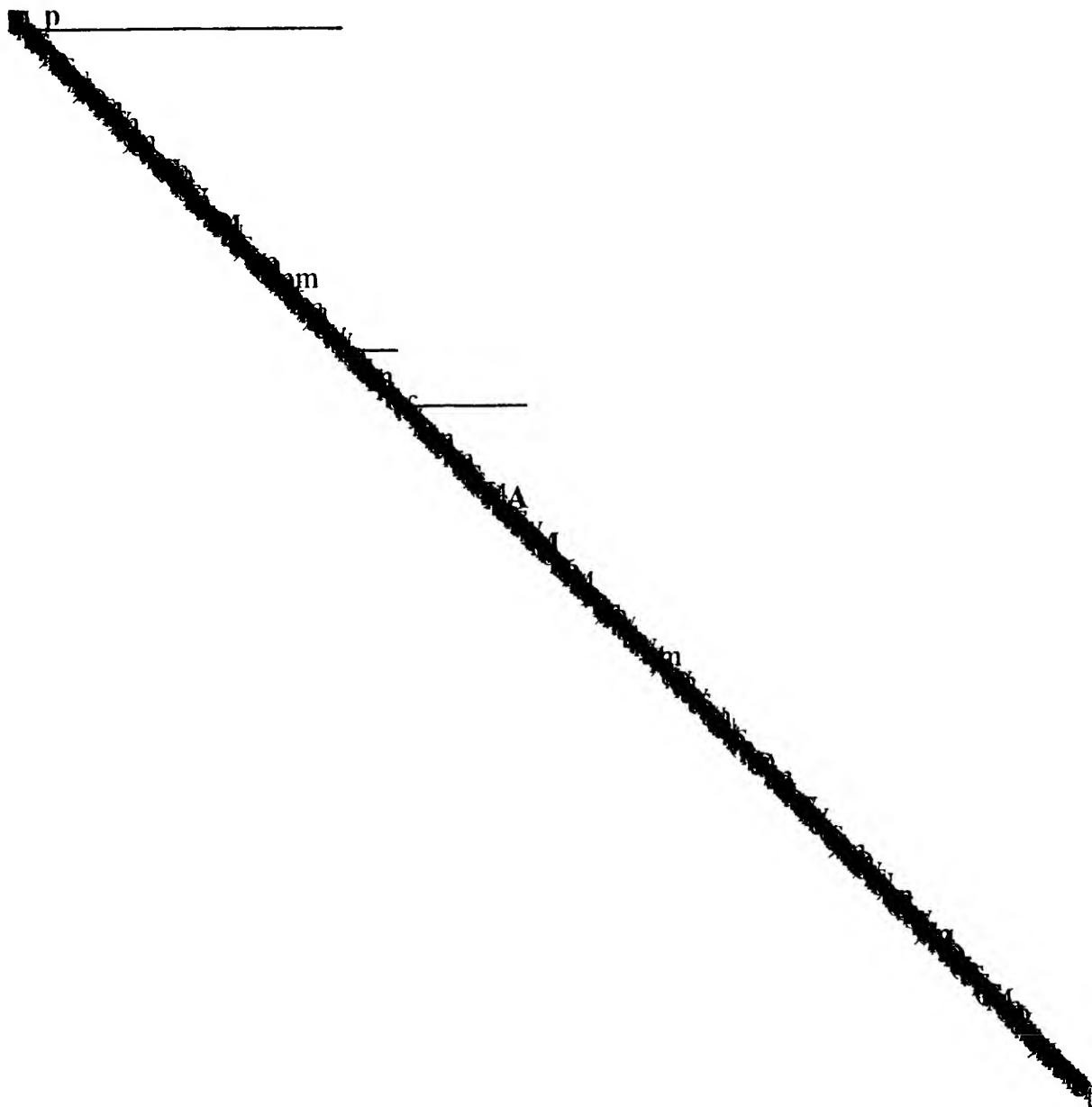


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$z_0$



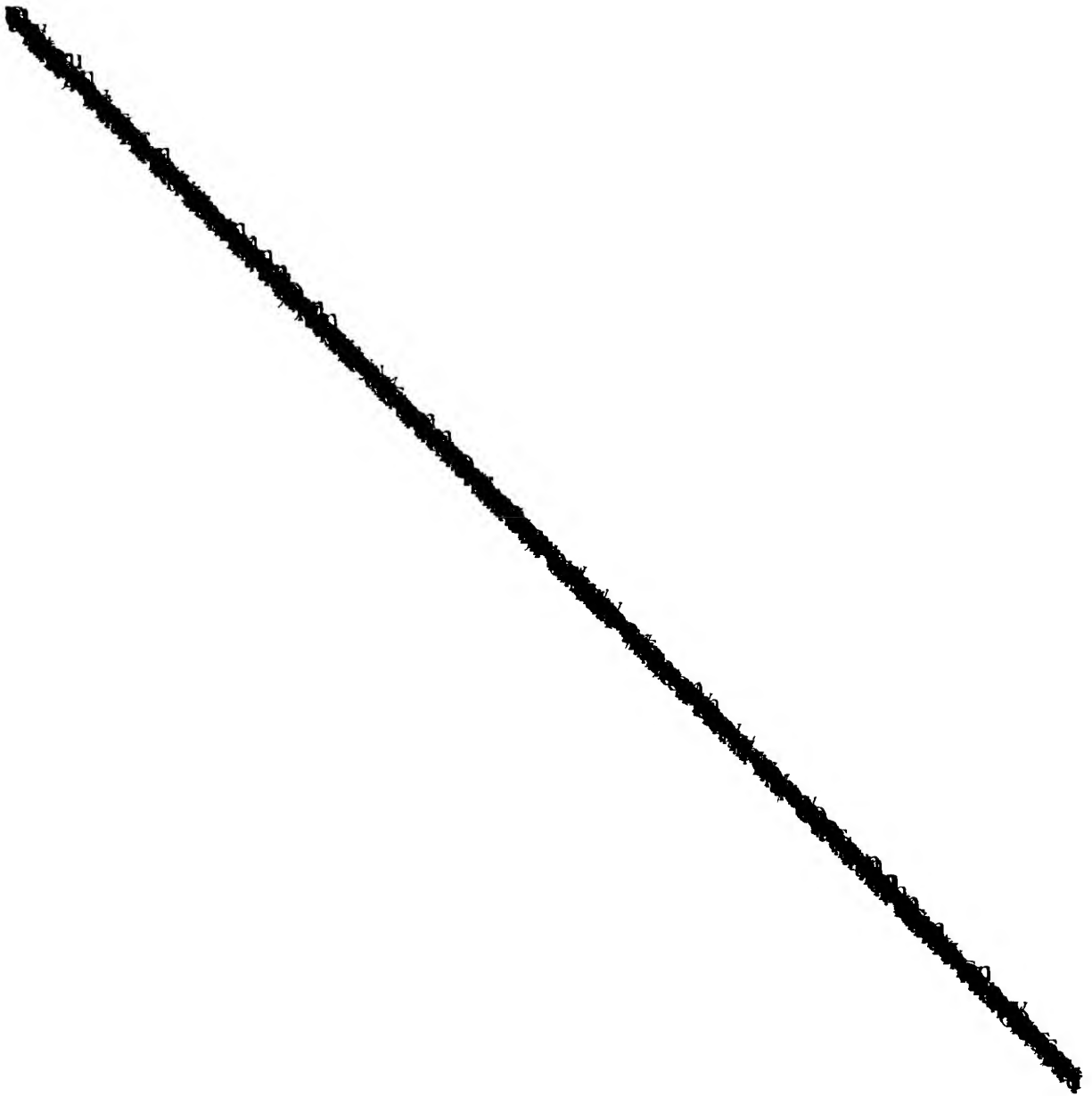


silver grains generated in the initial  $\text{Ag}^+$  reduction step was accomplished with a commercial silver enhancer solution (Sigma, Silver Enhancer Kit) which was further diluted with pure water when lower metal deposition rates were desired. Drops of the enhancer solution were placed on the template surface for the specified periods of time, then removed and the surface rinsed with drops of pure water. The removal of the drops was done by suction with a sharp pipette without any visible traces of liquid being left on the surface, due to the relatively high hydrophobicity of the TFMS surface. Thus, the water contact angles characteristic of TFMSs obtained from mixed precursor monolayers with a molar ratio NTS/OTS = 1/2 vary from ca. 70°(adv.) and 64° (rec.) on the silver-free surface, to ca. 67° (adv.; rec.) on the surface fully loaded with  $\text{Ag}^+$  ions.

The post-patterning chemical modification and self-assembly operations involving liquid reagents were done with drops of the desired solution being placed on the patterned monolayer surface (without removing the sample from the microscope stage), followed by drops of a suitable rinsing solvent. For the self-assembly of the NTS overlayer (Figs. 1, 4-6), a drop of water was first placed on the surface for ca. 2 min, then a drop of a 5 mM solution of NTS in BCH (for ca. 2 min), and final rinse with two drops of pure BCH followed by two drops of decalin, the NTS adsorption and the solvent rinses being repeated twice. Since none of the liquids employed wet the OTS monolayer, removal of the drops was simply done by suction, without any visible traces of material being left on the surface.

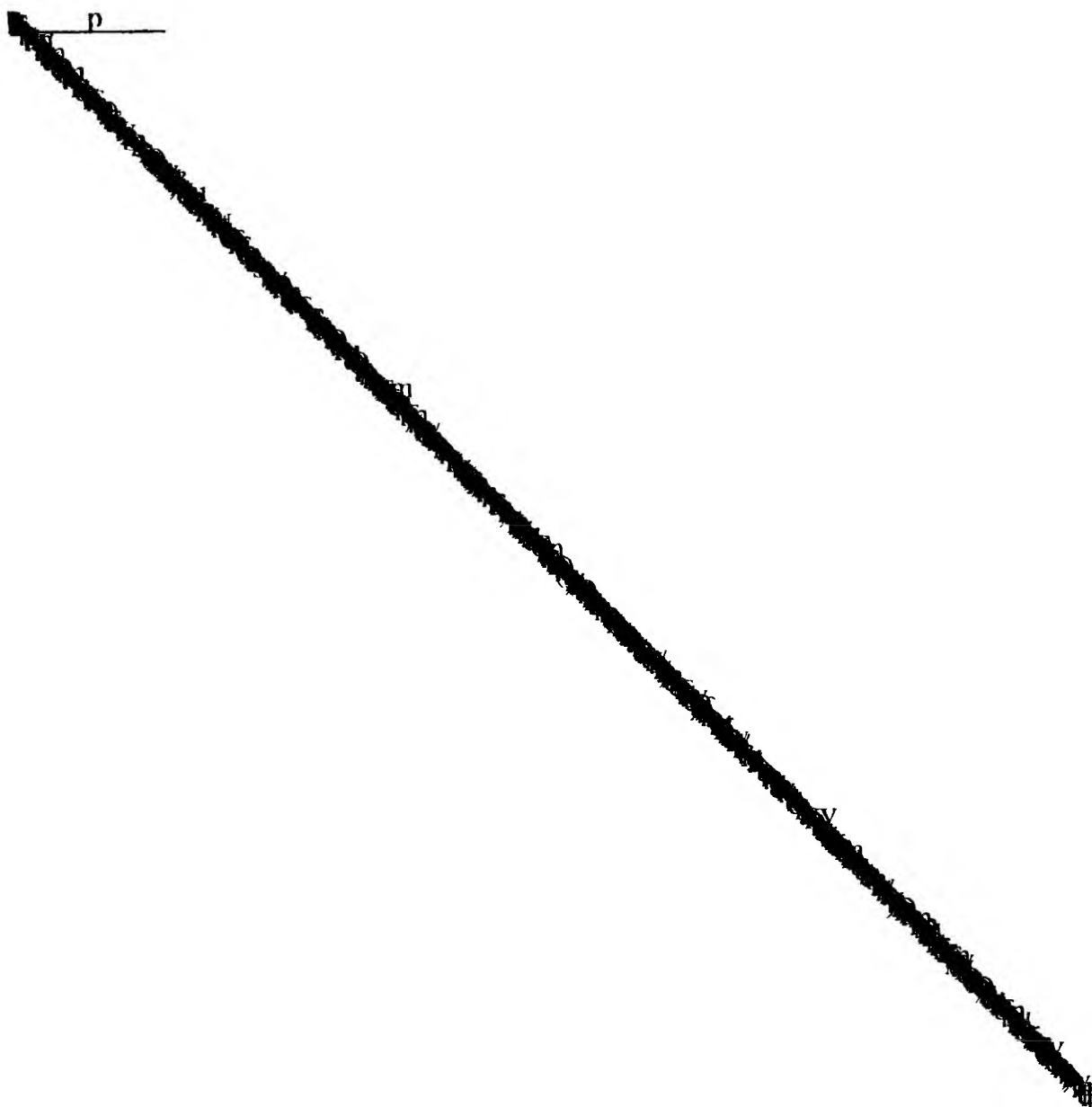
For the conversion of NTS to TFMS, the sample was irradiated (Hg lamp,  $\lambda = 254$  nm) for 10 min in a  $\text{H}_2\text{S}/\text{Ar}$  (1:1) atmosphere, then rinsed with pure argon and finally twice sonicated (for ca. 15s each) in pure toluene. Both the NTS and TFMS overlayers successfully withstand Scotch tape peeling, which was routinely applied in order to improve the AFM images by removal of adventitious contamination from the surface. For the formation of CdS, the TFMS surface was loaded with  $\text{Cd}^{2+}$  ions from a 1 mM solution of cadmium acetate in water (2 min adsorption, followed by rinse with two drops of pure water) and then exposed for 10 min to the same  $\text{H}_2\text{S}/\text{Ar}$  atmosphere (without irradiation) followed by the argon rinse. The deposition of

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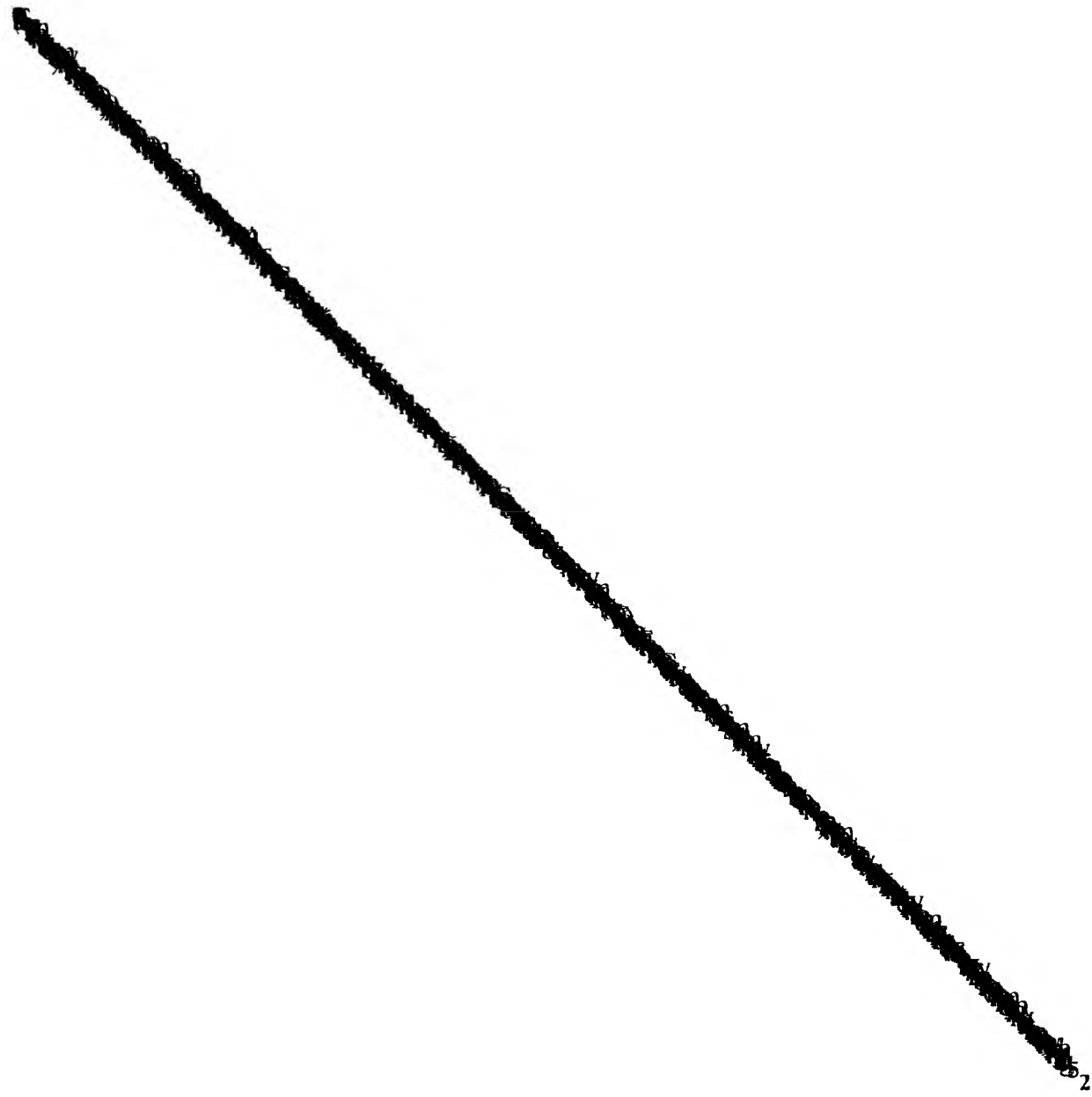


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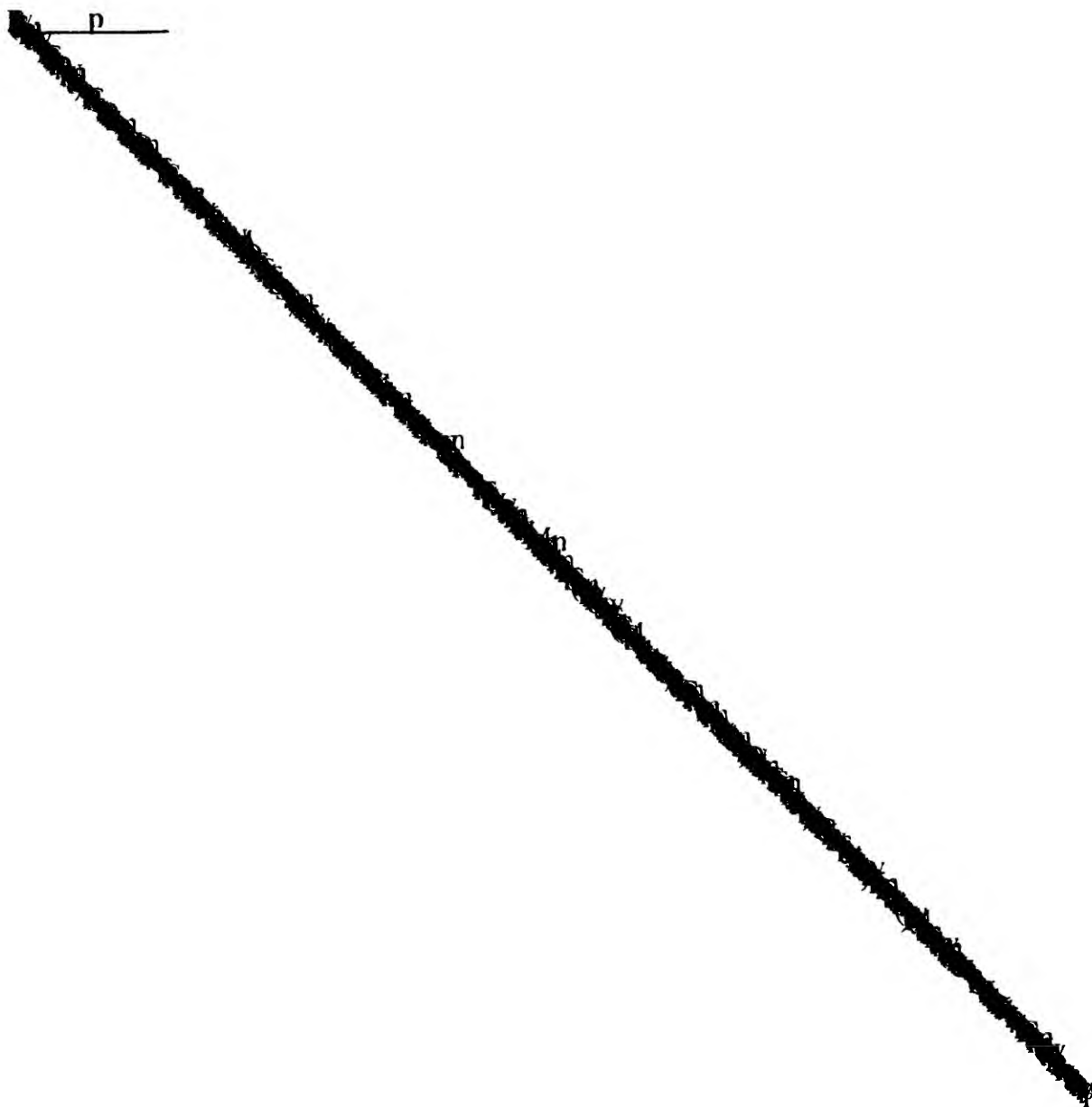
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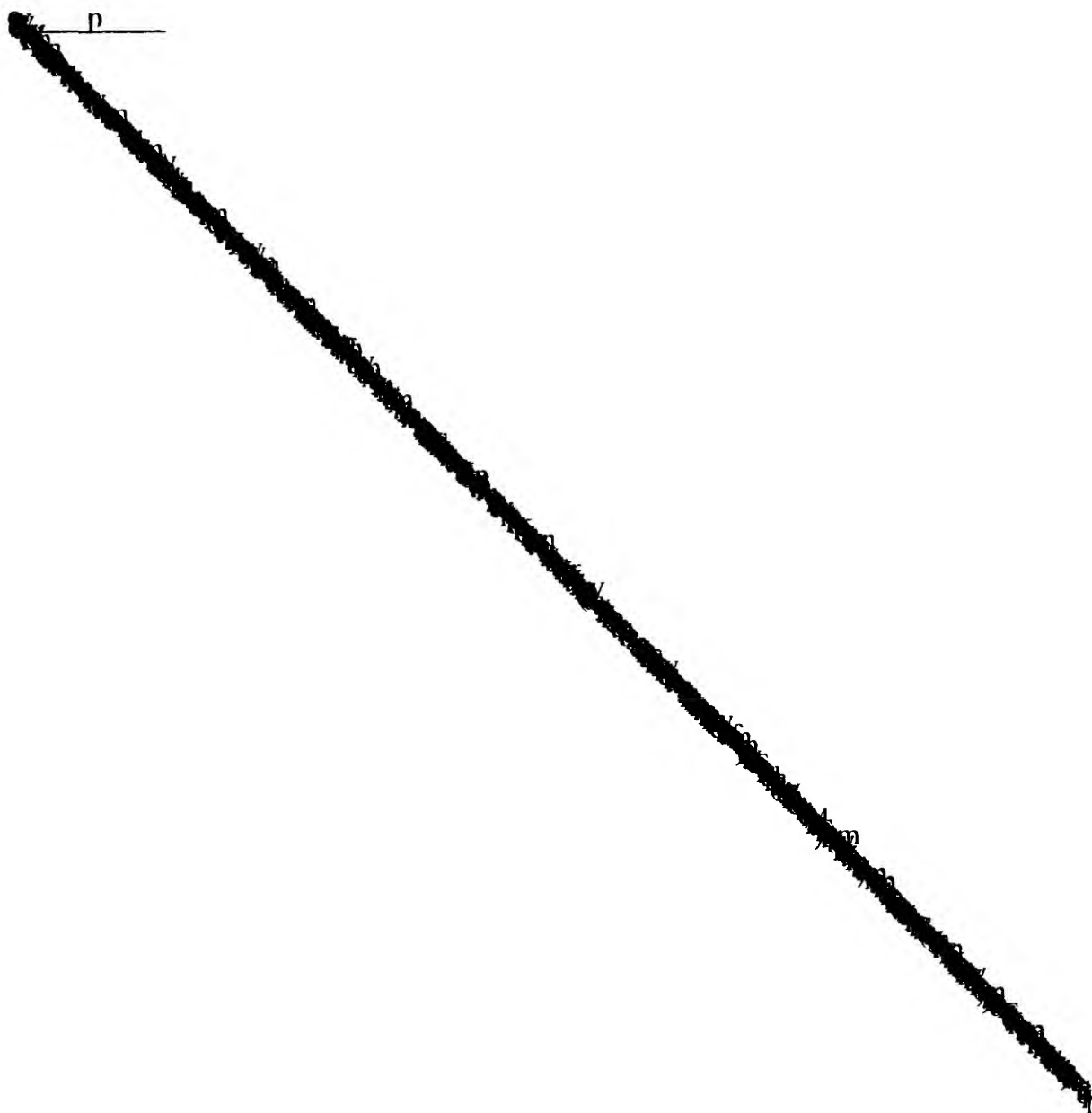
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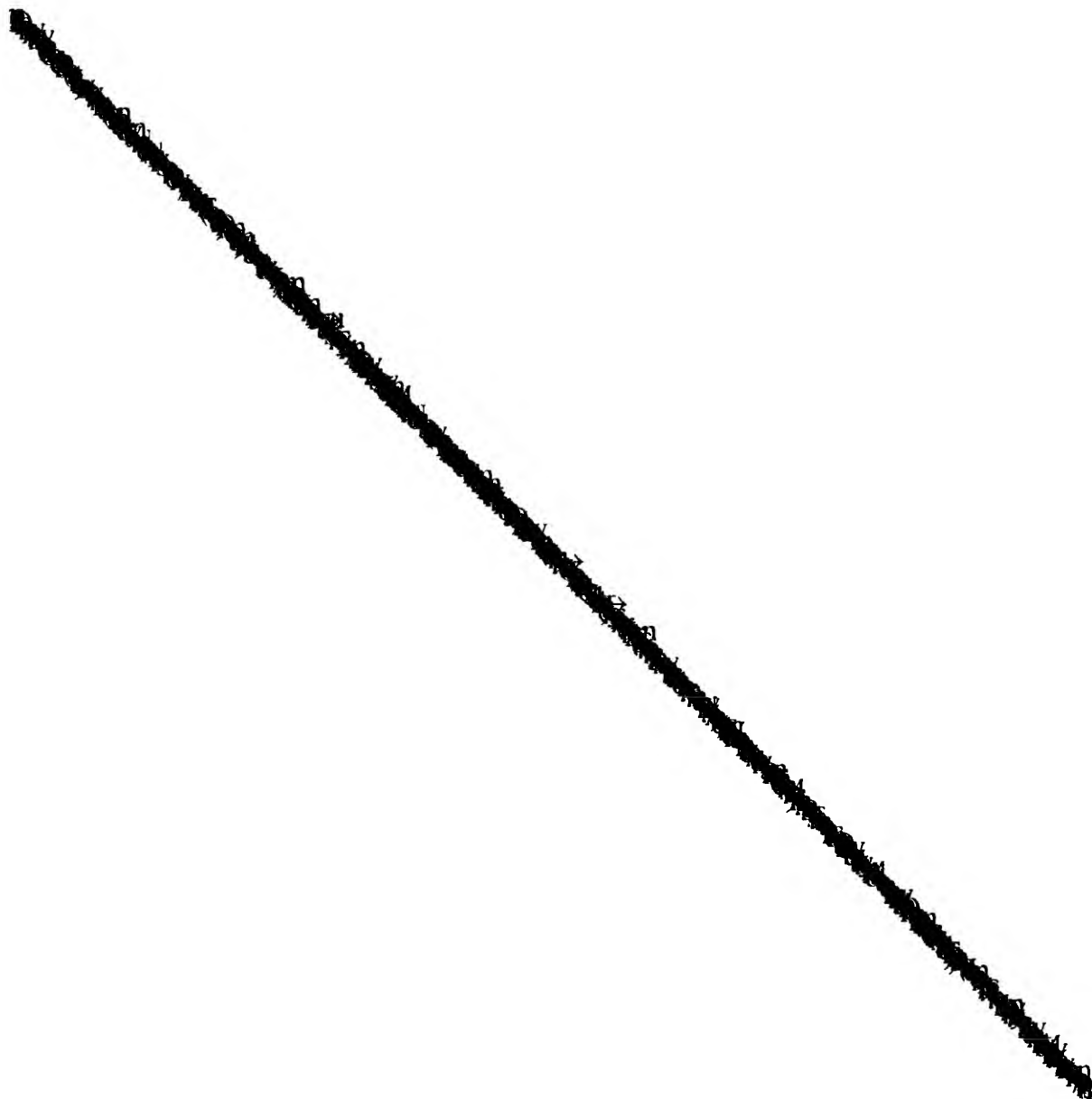
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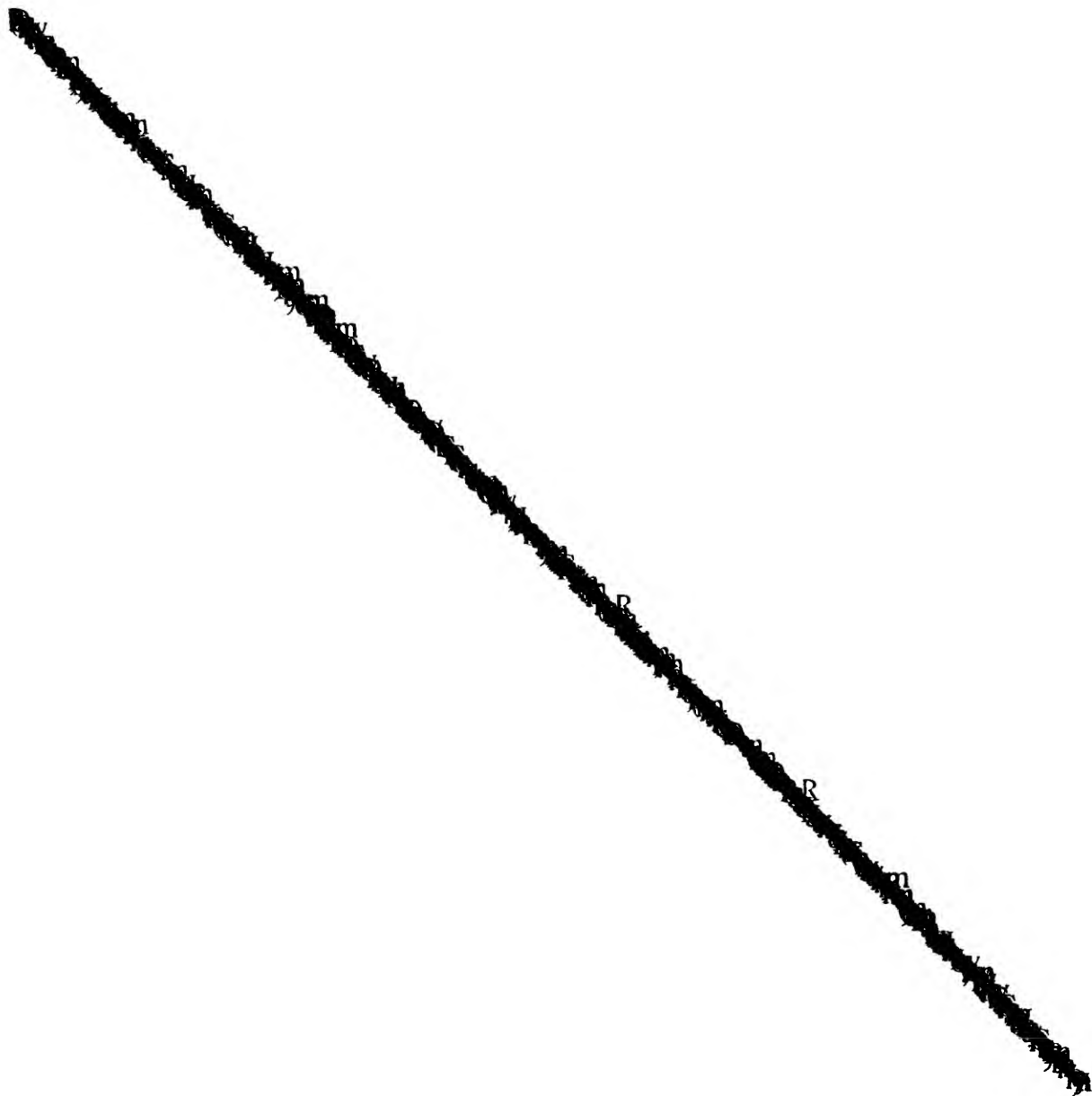
A line graph showing the relationship between the number of people ( $n$ ) and the number of handshakes ( $H$ ). The x-axis is labeled  $n$  and ranges from 0 to 10. The y-axis is labeled  $H$  and ranges from 0 to 45. A series of points are plotted at  $(1,0)$ ,  $(2,1)$ ,  $(3,3)$ ,  $(4,6)$ ,  $(5,10)$ ,  $(6,15)$ ,  $(7,21)$ ,  $(8,28)$ ,  $(9,36)$ , and  $(10,45)$ . A straight line is drawn through these points, starting from the origin  $(0,0)$ .



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23. A method for the production of hybrid metal-organic nanostructures according to claim 18, by template-controlled self-assembly strategy, comprising:

(i) assembling a monolayer of a silane compound terminated by a functional group such as -SH and/or -S-S- on a solid substrate;

5 (ii) binding a metal ion such as  $\text{Ag}^+$  to the functional group of (i); and

(iii) non-destructively patterning the top surface of said metal ion-terminated layer of (ii) by means of an electrically biased conducting scanning probe device, stamping device and/or liquid metal or metal alloy or any other device that can touch said organic monolayer surface and inscribe therein a chemical  
10 modification pattern upon application of an electrical bias, thus forming the pattern by site-defined reduction of the metal ions to elemental metal particles.

24. The method according to claim 23, which comprises further developing the elemental metal particles to form self-assembled metal islands or metal films.

15 25. A method for the production of hybrid inorganic-organic or organic-organic nanostructures according to claim 18, by template-controlled self-assembly strategy, comprising:

(i) assembling a monolayer of a silane compound terminated by a methyl group, on a solid substrate;

20 (ii) non-destructively patterning the top surface of said methyl-terminated layer of (i) by means of an electrically biased conducting scanning probe device, stamping device and/or liquid metal or metal alloy or any other device that can touch said organic monolayer surface and inscribe therein a chemical modification pattern upon application of an electrical bias, thus forming the pattern by  
25 electrochemical site-defined oxidation of the terminal methyl group, for example to an oxygen-containing group such as  $\text{COOH}$ , and optionally further chemically modifying this oxidized methyl site to another functional group; and

(iii) further generating or binding a metal, metal compound, organic metal or conducting polymer at the modified surface sites of said organic layer of (ii), thus  
30 obtaining said nanostructures with a combination of a metal, metal compound,

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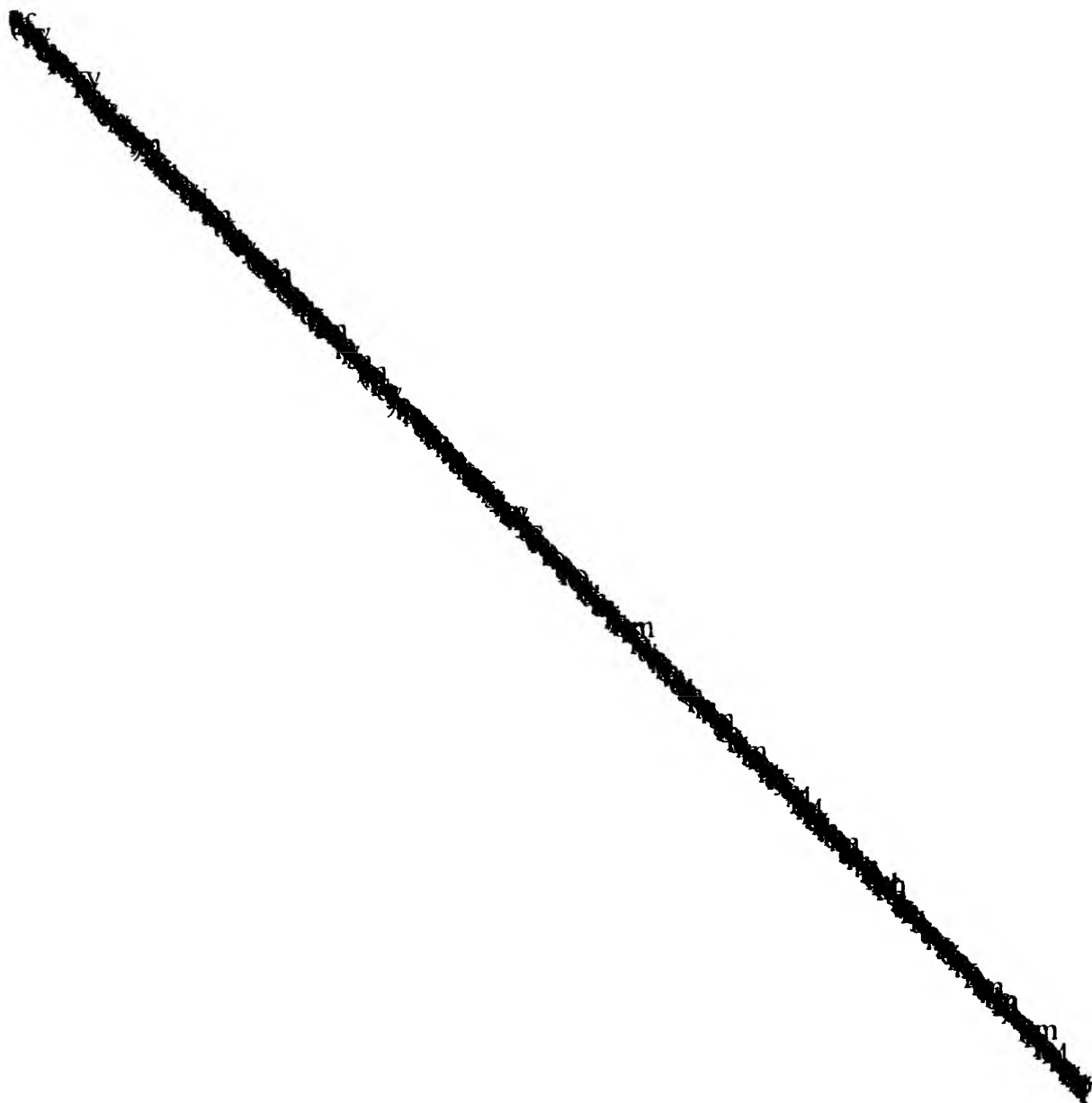


FIG. 1

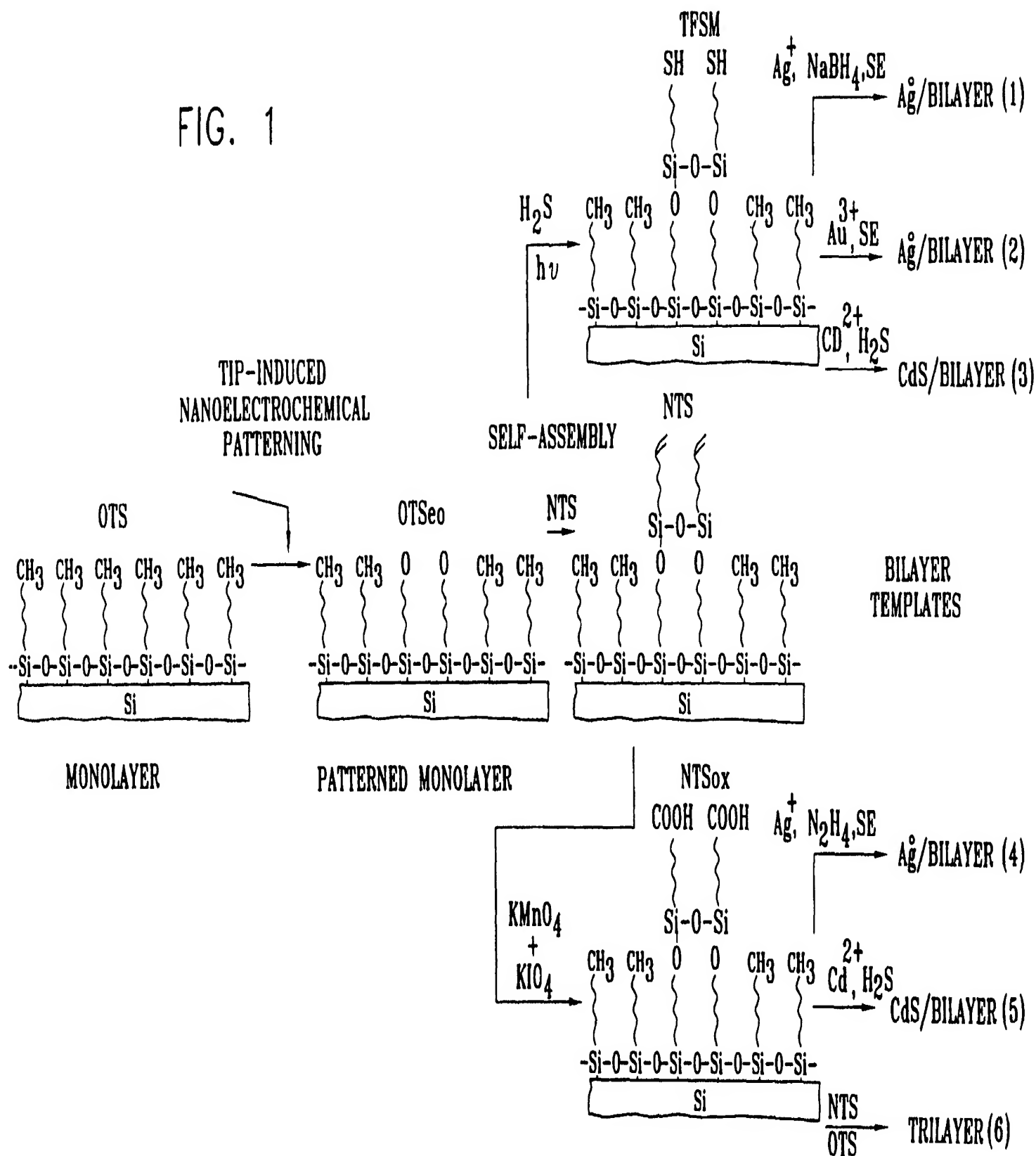
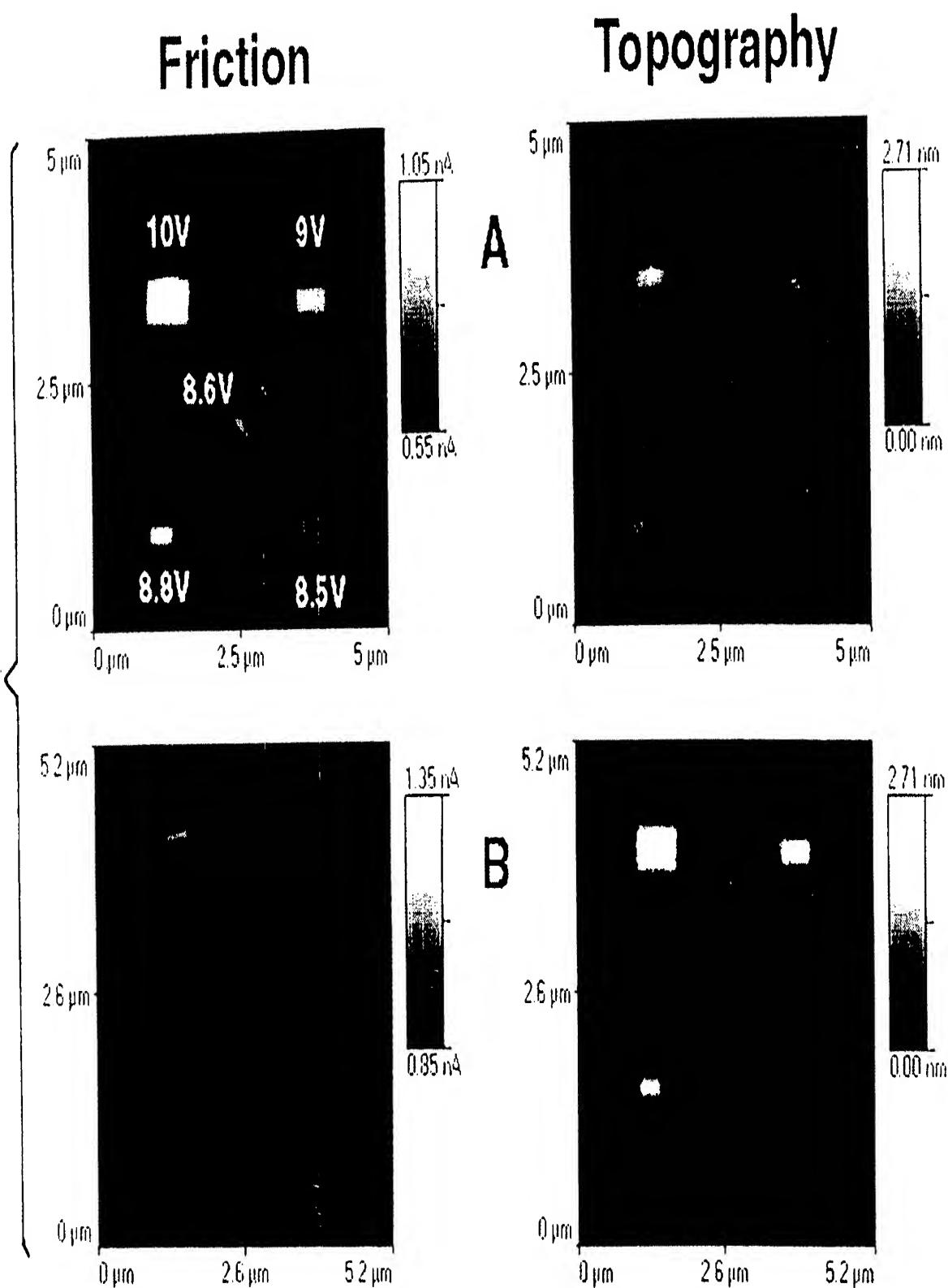
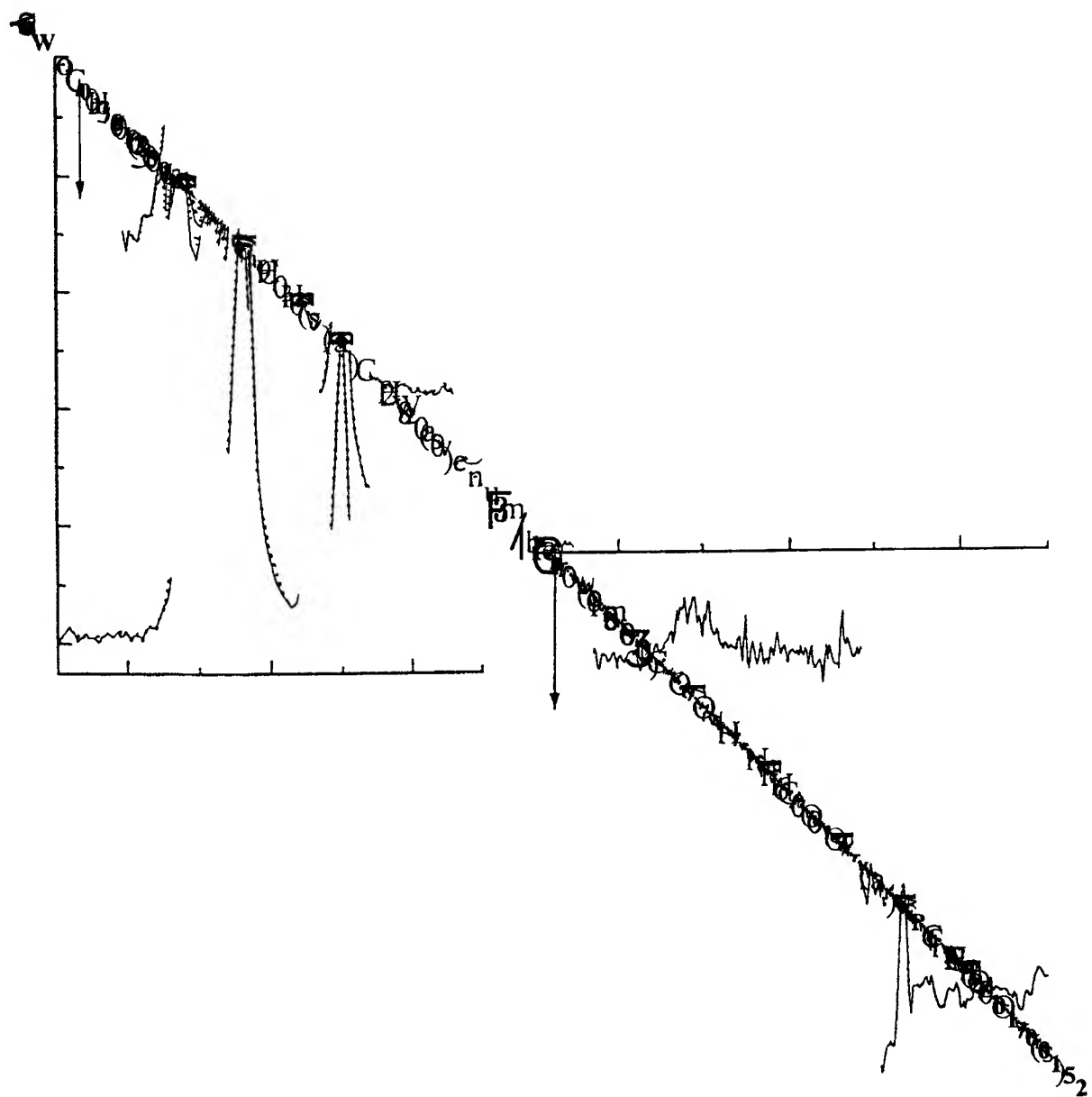


FIG. 2



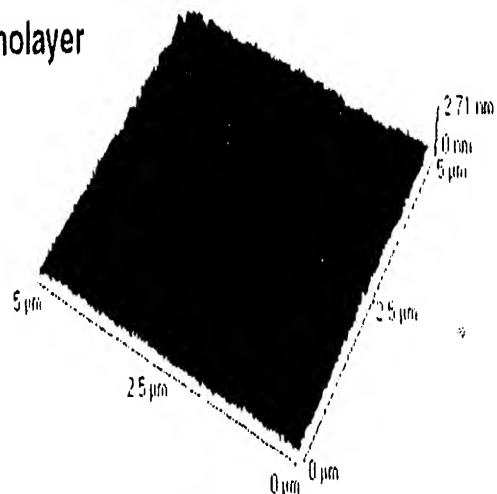
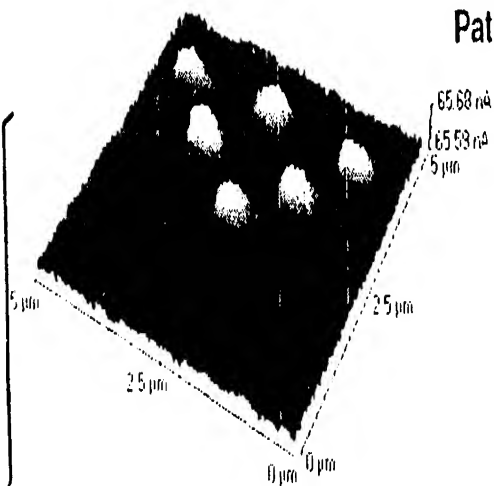


Friction

Topography

OTSeo  
Patterned Monolayer

(1)



NTS/OTSeo Bilayer

(2)

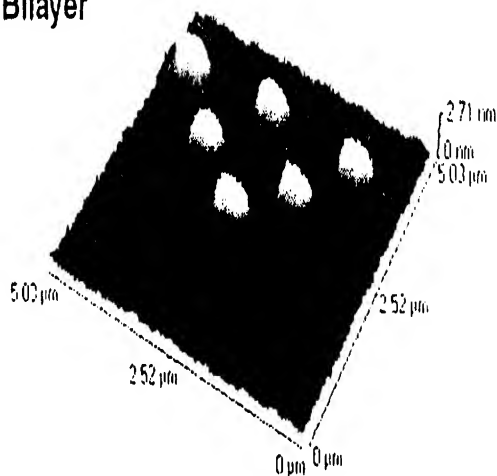
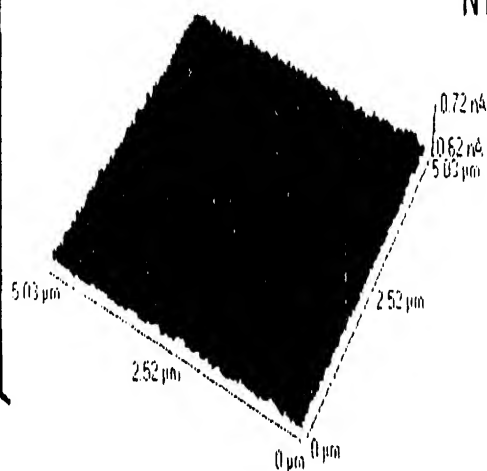
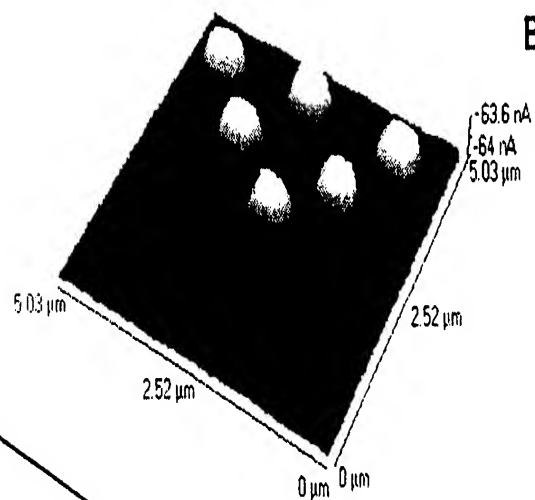


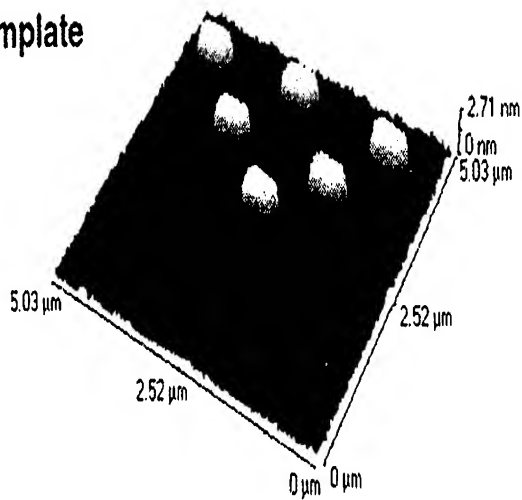
FIG. 4A



TFSM  
Bilayer Template



(3)



Ag / Bilayer

(4)

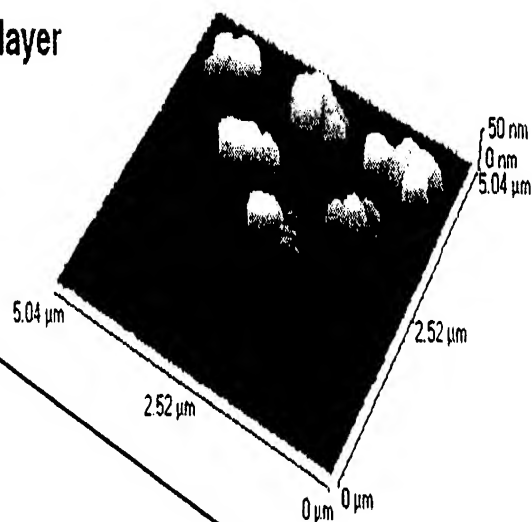


FIG. 4B

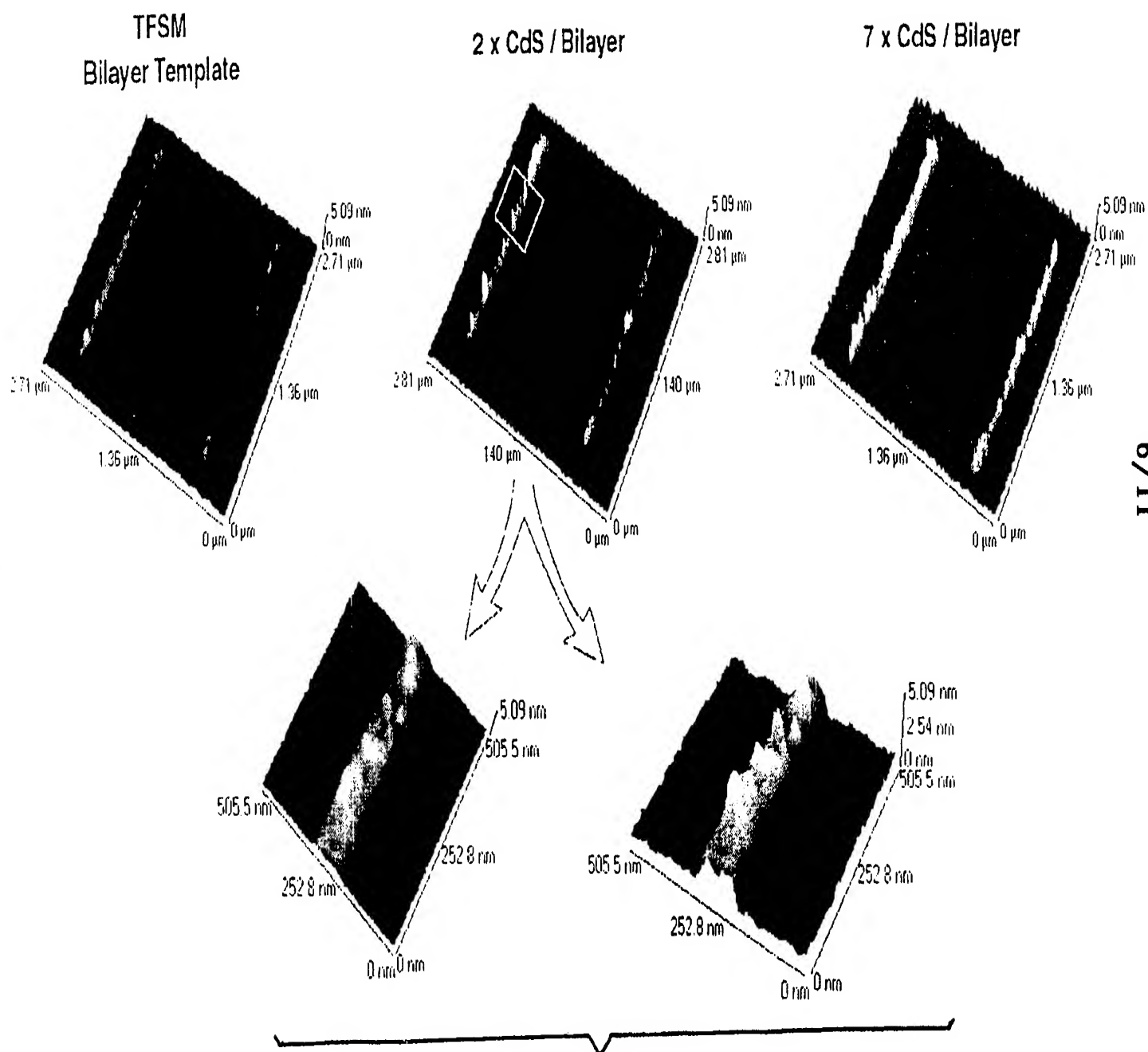


FIG. 5

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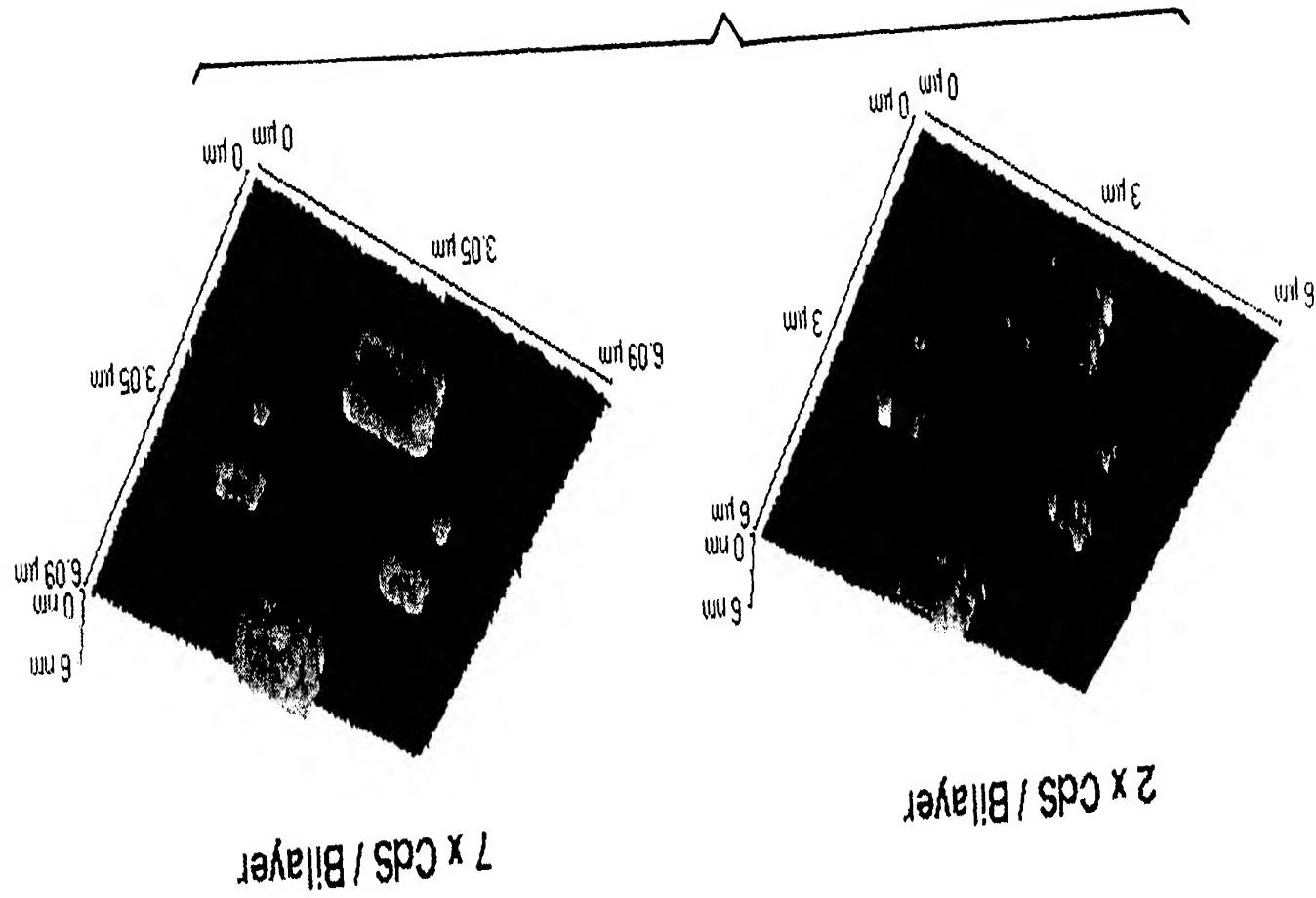


FIG. 6

FIG. 7

(AFM)  
NANOELECTROCHEMICAL REDUCTION

SELF-ASSEMBLED  
SILVER ISLAND

TFSM

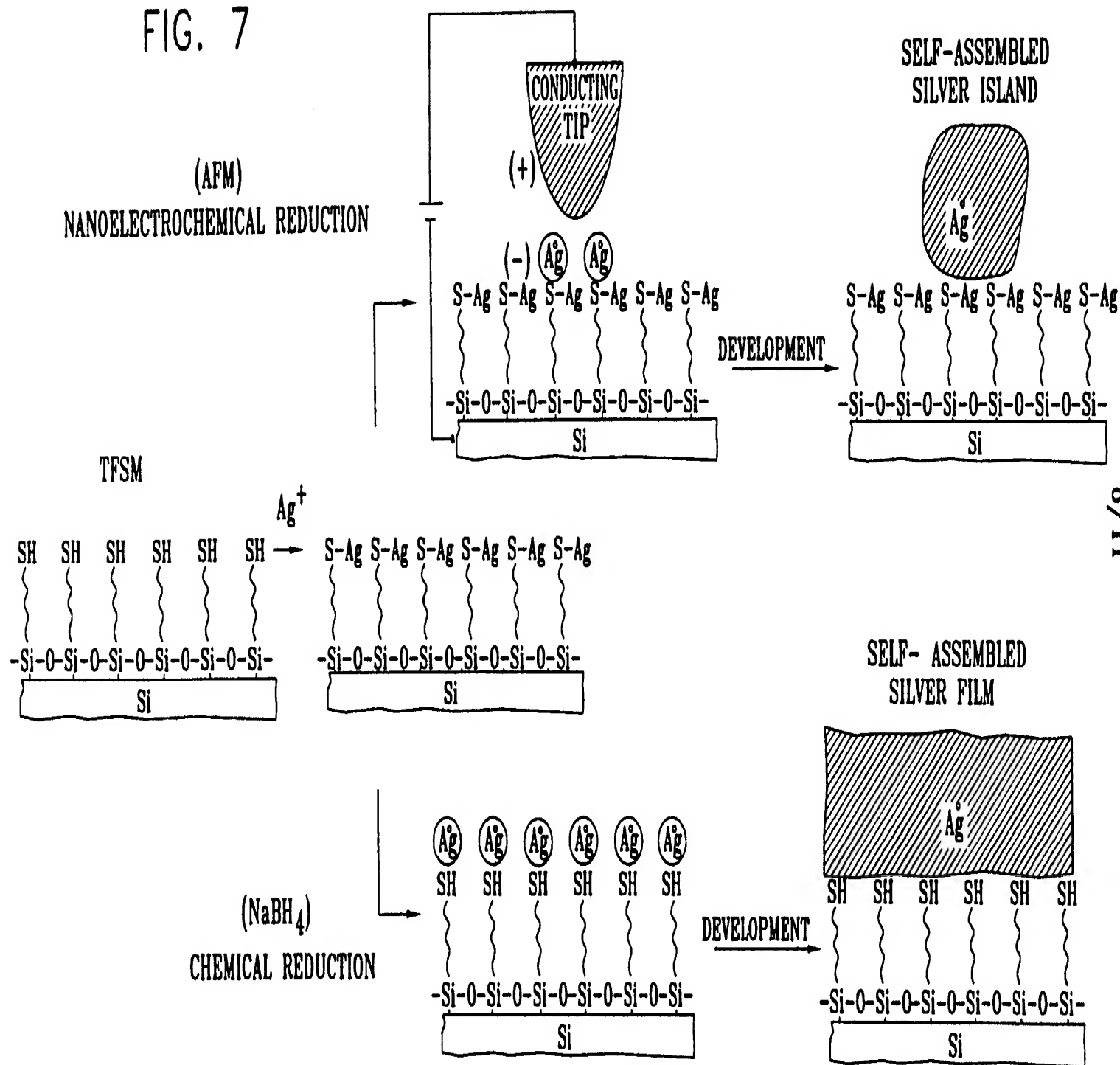
DEVELOPMENT

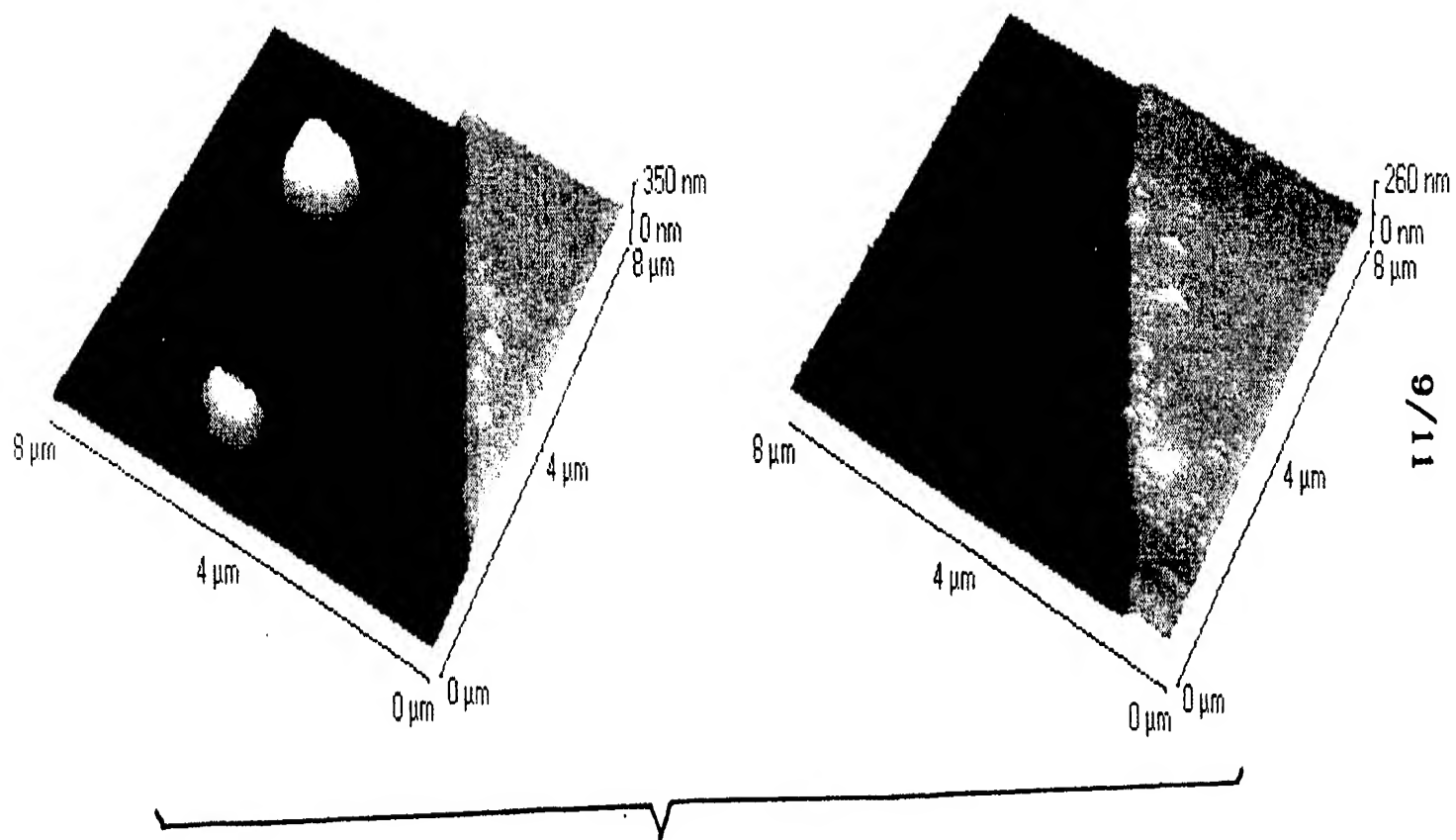
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SELF- ASSEMBLED  
SILVER FILM

( $\text{NaBH}_4$ )  
CHEMICAL REDUCTION

DEVELOPMENT





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FIG. 8

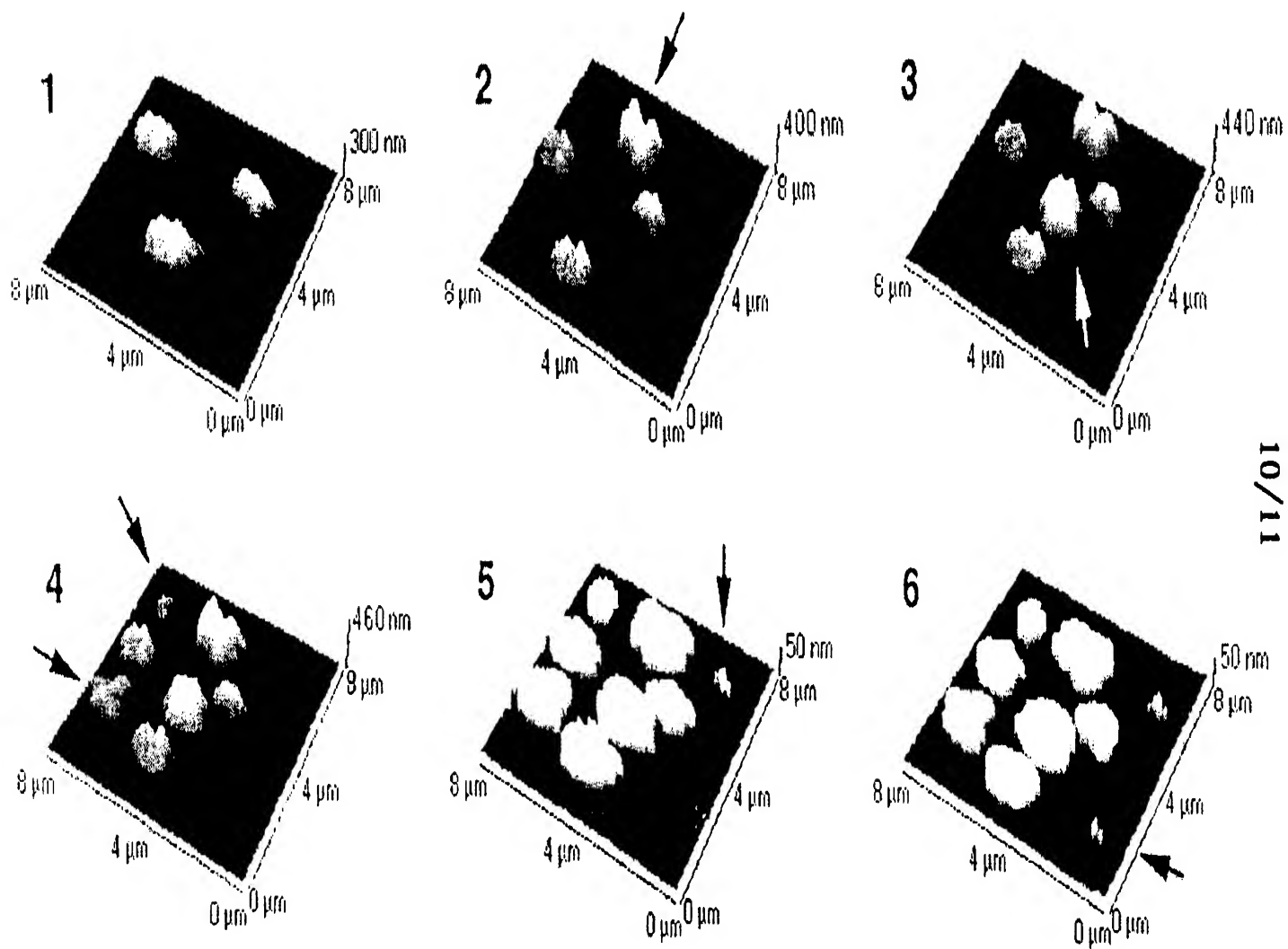
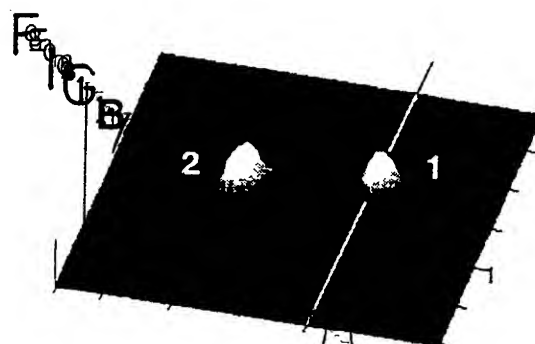
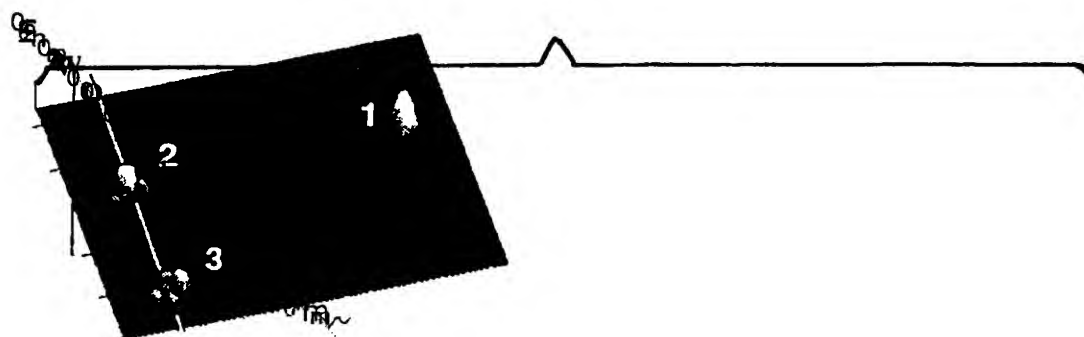


FIG. 9



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